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LARGE SCALE LABORATORY PREPARATION OF 1,3,5-TRINITRO-2,4,6-TRIBROMOBENZENE

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U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

LARGE SCALE LABORATORY PREPARATION OF 1,3,5-TRINITRO-2,4,6-TRIBROMOBENZENE

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ABSTRACT: Several pounds of 1,3,5-trinitro-2,4,6-tribromobenzene were prepared by nitrating 1,3-dinitro-2,4,6-tribromobenzene with a mixture of potassium nitrate and fuming sulfuric acid at 125°C.

1,3-dinitro-2,4,6-tribromobenzene was prepared by nitration of sym-tribromobenzene with a mixture of fuming nitric acid and concentrated sulfuric acid at 60°C.

This procedure was am improvement over previous methods, as only commercially available materials were used, less time was required, and the yield was raised over two-fold.

Explosives Research Department
U.S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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This report is a description of an improved procedure for the synthesis of 1,3,5-trinitro-2,4,6-tribromobenzene. The work was performed under Task NOL-Re2c-19-1-53. The reliability of the work and validity of the conclusions are the responsibility of the author and of the Chemistry Division, Explosives Research Department of the Naval Ordnance Laboratory. This report is for information only.

EDWARD L. WOODYARD
Captain, USN
Commander

PAUL M. FYE
By direction

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INTRODUCTION

1,3,5-Trinitro-2,4,6-tribromobenzene, hereafter designated as s-trinitrotribromobenzene, was first prepared on a 0.05 mole scale in 1888 by Jackson and Wing (1) by nitration of 1,3,5-tribromobenzene in two steps. 1,3-Dinitro-2,4,6-tribromobenzene, hereafter designated as s-dinitrotribromobenzene, was obtained by heating 1,3,5-tribromobenzene with absolute nitric acid for a few hours. s-Trinitrotribromobenzene was prepared in 20-40% yield by treating only 20 g of the dinitro compound with a mixture of 760 g absolute nitric acid and 380 g of fuming sulfuric acid at the boiling point for five hours. The crude product was purified by boiling with alcohol and recrystallization from chloroform. This procedure was followed by Mr. Francis Taylor (2) of this laboratory who prepared 200 g of s-trinitrotribromobenzene. He obtained yields of 60-70% in the preparation of s-dinitrotribromobenzene and 40-45% in the preparation of s-trinitrotribromobenzene. There was a considerable amount of decomposition in the final step. The analogous halogen compound, s-trinitrotrichlorobenzene, has been prepared by sulfonation of 1,3,5-trichlorobenzene and then nitration by fuming nitric acid for 30 hours at temperatures ranging up to 145°C (3).

The preparation of s-trinitrotribromobenzene according to Jackson and Wing (1) appeared to be difficult to adapt to larger scale production because of the large proportion of acid used and because of the need for absolute nitric acid. Also the oxidative conditions created by boiling nitric acid in sulfuric acid would seem to be detrimental to the yield of the desired compound. On a large scale a problem of handling the large amounts of decomposition gases would arise in the trinitration step. Therefore it was necessary to work out a high yield procedure which would be adaptable to expansion to the larger scale preparation of 98 mole per cent pure s-trinitrotribromobenzene. At the same time the procedure should not require excessive amounts of time and material.

This report contains a description of the preparation of s-dinitrotribromobenzene on a six pound scale using a mixture of nitric and sulfuric acid and of the preparation of s-trinitrotribromobenzene on a one pound scale by the use of potassium nitrate in fuming sulfuric acid. This procedure in less time and with ordinary commercially available materials improved the yield of product from 31% by previous methods to 74%, based on 1,3,5-tribromobenzene.

RESULTS AND DISCUSSION

Preparation of s-Dinitrotribromobenzene

In spite of the deactivating influence of halogen atoms on an aromatic compound, in 1,3,5-tribromobenzene the singular position of the three bromine atoms ortho, ortho and para to the three open positions should aid substitution in at least one and possibly two of the open positions without using drastic conditions. Under the conditions Jackson and Wing used, the mono derivative was difficult to obtain and the dinitro derivative invariably was formed (1). Also Backer and Van der Baan (4) prepared 1,3-dinitro-2,4,6-trichlorobenzene in 80% yield by heating 1,3,5-trichlorobenzene in a mixture of nitric acid (density 1.52) and absolute sulfuric acid.

By using a mixture of commercial fuming nitric acid and concentrated sulfuric acid, the dinitration of 1,3,5-tribromobenzene occurred in nearly quantitative yield under very mild conditions. When 1 part of 1,3,5-tribromobenzene was added to a mixture of 1.8 parts of ordinary concentrated sulfuric acid (96%) and 4.5 parts of commercial white fuming nitric acid (density 1.49, assay 95%) at room temperature nitration began immediately and the temperature of the solution rose to 75°C. After 10 minutes the temperature of the mixture was allowed to recede to 70°C and then held at 70°C for 5 minutes. If the temperature of the reaction mixture was maintained too long after the heat from the reaction receded, gas would begin to evolve and the yield and purity decreased. When 1,3,5-tribromobenzene was added to the acid at 60°C nitration was very rapid and complete within a few minutes. The product was isolated by pouring the cooled reaction mixture over crushed ice, filtering, washing until free of acid, and drying. The nearly pure s-dinitrotribromobenzene obtained by this method was used for the trinitration step without further purification. The procedure worked equally well for all sizes of runs ranging from 1 gram to 2800 grams without complications. The results of the various experiments are summarized in Table I.

Since the above procedure worked so well, conditions for the reaction were not investigated except for an experiment where a mixture of 1.8 parts ordinary concentrated sulfuric acid and 3.0 parts white fuming nitric acid was used to nitrate 1 part of 1,3,5-tribromobenzene. The yield was 94% of less pure s-dinitrotribromobenzene than before.

Physical Properties of s-Dinitrotribromobenzene

Melting point	191.6°C (cor.)
Crystal density	2.53
Impact sensitivity (50% point, 2 1/2 kg wt)	320 cm
Vacuum stability	Excellent

TABLE I

DINITRATION OF 1,3,5-TRIBROMOBENZENE

Expt. No.	Amt. TBB	Amt. HNO_3	Amt. H_2SO_4	Reaction Time	Reaction Temp	% Yield	M.P.
8	1.0 g	4.5 g	1.8 g	15 min. 30 min.	70°C 90°C*	92	192°
9	0.94 g	4.5 g	1.8 g	15 min. 30 min.	77°C 100°C*	97	188°
10	3.14 g	15.0 g	7.4 g	10 min.	30-62°C	100	191°
13A	31.0 g	155 g	62 g	30 min.	30-75°C	100	191°
13B	31.0 g	155 g	62 g	30 min.	30-75°C	100	192°
15A	94.0 g	465 g	186 g	30 min.	55-65°C	97	191°
15B	100.0 g	454 g	186 g	30 min.	55-65°C	100	191°
18B	300 g	908 g	558 g	45 min.	60-65°C	94	191°
24	1500 g	4540 ml	1500 ml	50 min.	20-65°C	98	192°
26	2800 g	8400 ml	2800 ml	45 min.	20-65°C	99	192°

* Decomposition gases appeared during this period.

Preparation of s-Trinitrotribromobenzene

Because of the difficulty encountered by previous workers in nitrating s-dinitrotribromobenzene by mixed nitric and sulfuric acids and because of the decomposition experienced on prolonged heating in the preparation of the dinitro compound this method of nitration was not further investigated. However, the use of nitrate salts and sulfuric acid has been successful in nitrating compounds which are not nitrated by mixed acid. This system appeared worthy of investigation because anhydrous conditions are easily obtained, no nitrogen oxides are introduced and a high reaction temperature can be obtained without decomposition of the nitrating agent (5). Preliminary experiments showed that nitration by the use of sodium or potassium nitrate and fuming sulfuric acid was feasible. Consequently, this method was developed for the preparation of s-trinitrotribromobenzene.

The investigation of the procedure followed two courses. First an effort was made to obtain an initial product of sufficient purity that recrystallization would not be necessary. Upon failure to achieve this goal the initial product was purified by recrystallization from chloroform. In the best nitration procedure the optimum molar ratio of s-dinitrotribromobenzene to potassium nitrate to sulfur trioxide was found to be 1 to 4 to 9.5.

The reaction vessel was charged with 30% fuming sulfuric acid and the potassium nitrate was added with stirring and cooling to keep the solution below 65°C. Then the solution was heated to 110°C and the s-dinitrotribromobenzene added rapidly. The temperature was raised to 125°C and held until a faint color of bromine appeared, 7 - 9 hours. The reaction mixture was cooled rapidly to 20° - 25°C and then poured slowly onto crushed ice. The product was washed free of acid, dried and recrystallized from chloroform.

An investigation of the optimum conditions was undertaken before large scale preparations were attempted by study of the effect of varying the temperature and the molar ratios of the reactants. The progress of the reaction was followed by comparing the melting point of samples withdrawn at intervals with a mixed melting point curve of the di- and trinitro compounds, Figure 1. The first aim of obtaining a nearly pure initial product could not be reached. Long reaction periods were necessary to raise the melting point of the product to the neighborhood of 296°C, the melting point of pure s-trinitrotribromobenzene. Also regardless of conditions, after a few hours a red-brown gas was slowly evolved which was found to be not oxides of nitrogen but bromine. By varying the reactant ratios, an effort was made then to eliminate the appearance of the bromine, which was indicative of a detrimental side reaction. However, the bromine invariably appeared coincidentally with disappearance of the eutectic melting point of dinitro- and trinitrotribromobenzene. The disappearance of the eutectic melting point was taken as an indication that little of the dinitro compound was left to nitrate.

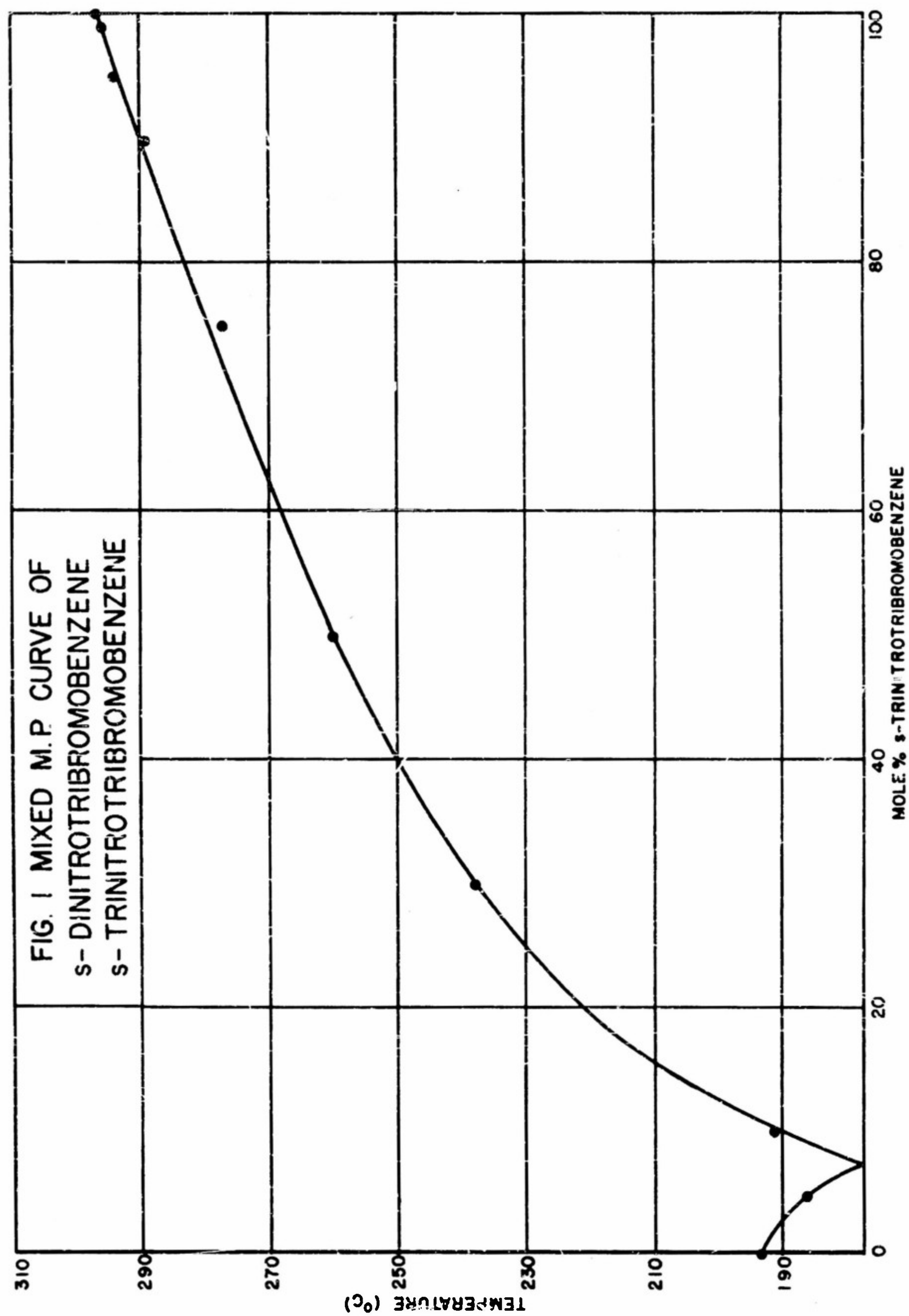

FIG. I MIXED M.P. CURVE OF
s- DINITROTRIBROMOBENZENE
s- TRINITROTRIBROMOBENZENE

In the investigation of a method of purifying the crude product some crystals melting at 234-5°C were isolated. Elemental analysis indicated that they were crystals of a eutectic of s-trinitrobribromobenzene and 1,2,3,5-tetrabromo-4,6-dinitrobenzene, hereafter designated as s-tetrabromodinitrobenzene. Other side reaction products were obtained which melted in the range of 163-180°C and have not yet been identified. Jackson and Wing also isolated s-tetrabromodinitrobenzene from their crude reaction product and gave evidence that the source of the bromine for this side reaction was s-dinitrotribromobenzene (1). That a small amount may come also from s-trinitrotribromobenzene was found by heating this compound in the nitration mixture at 130°C. After six hours the s-trinitrotribromobenzene melting point decreased from 297°C to 283°C - 290°C, and the weight of the sample decreased 6%. This indicated that it was necessary to nitrate at a temperature somewhat below 130°C. However, nitration at 110°C - 115°C extended the reaction period by 2 - 3 times, which could not be overcome by increasing the amount of potassium nitrate. High temperature favored the formation of s-tetrabromodinitrobenzene and decreased the yield of the trinitro compound. Long heating of the reaction mixture was also detrimental to yield. A reaction temperature of 120°C to 125°C was found to give a fair yield of the trinitro compound in 6 to 9 hours reaction time.

The rate of nitration increased with increased concentration of potassium nitrate up to a ratio of four moles of the nitrate to one of s-dinitrotribromobenzene. Beyond this concentration little effect was noted. The trinitration experiments are summarized in Table II.

The optimum concentration of potassium nitrate relative to fuming sulfuric acid was not investigated other than to assure complete utilization of the nitrate to give NO_2^+ ions. Millen and others (6) have given evidence that 12 weight per cent nitric acid in 35% oleum produces $(NO_2^+)(HS_2O_7^-)$ as the only solute, equation (1), and 21 weight per cent produces $(NO_2^+)(HSO_4^-)$ as the only solute, equation (2).

$$HONO_2+2H_2S_2O_7 = NO_2^{+}+HS_2O_7^{-}+2H_2SO_4 \qquad (1)$$

$$HONO_2+H_2S_2O_7 = NO_2^{+}+HSO_4^{-}+H_2SO_4 \qquad (2)$$

In concentrated oleum or in solutions more concentrated in nitric acid, reaction (2) is not complete. The potassium nitrate used in the s-dinitrotribromobenzene nitration corresponded to 10 weight per cent nitric acid in 30% fuming sulfuric acid. However, 1 mole of nitrate requires 3 moles of bisulfuric acid for complete conversion to NO_2^+ ions. In the nitration system that was used, only 2.3 moles of bisulfuric acid were available. Therefore, the potassium nitrate reacted with both bisulfuric and sulfuric acid, equations 3-6.

TABLE II

NITRATION OF DINITROTRIBROMOBENZENE

Expt. No.	Moles DNTBB	Moles KNO_3	Moles SO_3	Reaction Time hrs.	Reaction Temp, °C	Yield Recryst'd TNTBB %
17	0.01	0.07*	0.22	3	130-40	57**
19	0.03	0.21	0.56	21	125-35	53**
22	0.06	0.21	0.56	26	110-25	74**
29	0.45	1.6	4.4	7.5	125-30	56
34	0.52	1.9	5.0	7.5	130-1	63
36	0.12	0.15	0.56	16	131-2	48
39	0.09	0.23	0.84	5.8 1.5	131-2 126-8	59**
41	0.09	0.23	0.56	1 2.5 7	131-2 125-7 106-15	57
45	1.00	4.0	9.5	7	123-30	71***
47	1.12	4.5	10.0	9	125-7	73
48	1.12	4.5	10.0	9	125-6	74
46	0.80	4.8	10.0	18.5	109-13	70

* - Used $NaNO_3$ ** - Estimated *** - Lower melting residues contained 3-5% TNTBB

$$KNO_3+H_2S_2O_7=KHS_2O_7+HONO_2 \tag{3}$$

$$HONO_2+2H_2S_2O_7=NO_2^{+}+HS_2O_7^{-}+2H_2SO_4 \tag{4}$$

$$KNO_3+H_2SO_4=KHSO_4+HONO_2 \tag{5}$$

$$HONO_2+HS_2O_7^{-}=NO_2^{+}+2HSO_4 \tag{6}$$

These equations are consistent with the observation that no nitric acid distills at temperatures in excess of 90°C. After nitration was complete the reaction mixture did not fume at all. Reactions using a ratio of 3.7 moles sulfur trioxide to one of potassium nitrate did not result in improved yield.

Purification of the Crude Material

Previous workers purified their crude reaction products by first boiling the material with ethyl alcohol to remove unreacted s-dinitrotribromobenzene and side reaction products except s-tetrabromodinitrobenzene. The residue, consisting of s-tetrabromodinitrobenzene and s-trinitrotribromobenzene, was then recrystallized from chloroform. However, it was found that previous extraction was unnecessary and that the crude product could be recrystallized from chloroform directly. s-Tetrabromodinitrobenzene and the other components were much more soluble in chloroform than s-trinitrotribromobenzene which allowed a sharp separation. Even then large volumes of solvent and rehandling of crops were necessary in order to get the majority of the trinitro compound out of the crude material. Carbon tetrachloride did not give a good separation and benzene had to be paired with aqueous alcohol to be useful.

The following purification procedure was used for the large trinitration runs. The dry crude material was dissolved in slight excess of chloroform at the boiling point. The hot solution was filtered to remove dirt and after cooling to room temperature, the precipitated s-trinitrotribromobenzene was filtered. After further cooling the filtrate to -22°C, a second crop of 95% s-trinitrotribromobenzene was obtained. The second crop mother liquor was reduced by distillation to 25% of its original volume and then cooled. The third crop which separated contained about 31% s-trinitrotribromobenzene. The mother liquor of this crop was then evaporated to dryness. Second crops were combined and recrystallized once; third crops were combined and recrystallized twice. The low melting residues were not further handled though they contained a few per cent s-trinitrotribromobenzene.

Physical Properties of s-Trinitrotribromobenzene

Melting point	296°C (cor.)
Crystal density	2.39
Impact sensitivity (50% point)	118 cm
Vacuum stability	Excellent

EXPERIMENTAL

Preparation of s-Dinitrotribromobenzene

A 10 gallon stainless steel jacketed reaction kettle with a loose fitting lid and an efficient stirrer was charged with 8.4 liters of commercial fuming nitric acid (assay 95%) and 2.8 liters of concentrated sulfuric acid. After warming to 60° - 65°C, 2800 g 1,3,5-tribromobenzene was added over a period of 30 minutes. The temperature was held at 60° - 65°C for an additional 10 - 15 minutes and then lowered. A sample taken at this time melted at 191° - 192°C indicating complete nitration. The cooled reaction mixture was slowly poured into 40 liters of ice with good stirring. After standing for several hours, the supernatant acid solution was sucked off of the product, which was washed several times by decantation, filtered off and washed free of acid. After drying, the product weighed 3586 g, m.p. 191° - 192°C. The theoretical yield for the reaction is 3601 g.

A 1500 g run was made in the same manner except that the reaction mixture was heated at 70°C for a short period after the addition of 1,3,5-tribromobenzene. This caused gas evolution. The yield was 1896 g of the dinitro compound, m.p. 190° - 191°C, compared to 1929 g required by theory.

Preparation of s-Trinitrotribromobenzene

A three liter Pyrex resin reaction flask equipped with stirrer and thermometer was charged with 1510 ml of 30% oleum. A water bath was placed around the flask and 452 g of crystalline C.P. potassium nitrate was added at such a rate that the temperature was kept below 65°C. After the addition, the nitration mixture was clouded by potassium salts. The water bath was removed and the mixture was heated by a Glascol mantle for a 2 liter flask. At 95°C the solution was clear. At 110°C, 453 g of powdered s-dinitrotribromobenzene was added rapidly. The reaction mixture was held at 125° - 126°C for nearly nine hours at which time the faint red color of bromine vapor appeared. The heating mantle was removed and the mixture cooled rather rapidly, first by a hot water bath then by a cold water bath. The viscous mixture was poured slowly over 10 liters of crushed ice and then filtered, washed free of acid, and dried. There was obtained 483 g crude product, m.p. 270° - 288°C, compared with 503 g required by theory.

The dry crude product was dissolved in 6500 ml boiling chloroform and filtered hot to remove dirt. Upon cooling to room temperature, 235 g s-trinitrotribromobenzene, m.p. 296° - 297°C (cor.), was filtered off. The filtrate was cooled to -20°C for a few hours and 103 g, m.p. 293° - 296°C, was obtained. Recrystallization of the 103 g gave 97 g s-trinitrotribromobenzene and 5 g of a material melting at 250° - 260°C. The original mother liquor was reduced to 20% of its original volume by distillation. Crystallization of lower melting product did not occur until after 75% of the solvent had been removed. From the concentrated mother liquor 117 g of a mixture of compounds melting at 236° - 277°C was filtered at room temperature. This was recrystallized twice from chloroform, giving 37 g of s-trinitrotribromobenzene and 78 g of a mixture melting at 205° - 260°C. Evaporation of the third crop mother liquor left 26 g of residue, m.p. 170° - 225°C. The total of the combined crops of s-trinitrotribromobenzene was 269 g (73.2%). Lower melting material which still contained a small amount of s-trinitrotribromobenzene totaled 108 g, m.p. 170° - 260°C, accounting for 98.5% of the crude material.

NOTES

1. The appearance of red fumes of bromine indicates debromination and rebromination. The reaction should be stopped at this point as further heating merely increases the amount of low melting side products. One of these has been tentatively identified as 1,2,3,5-tetrabromo-4,6-trinitrobenzene, m.p. 232°C.

2. Lower temperatures (115°C) retard this debromination but require much longer reaction times (16 or more hours) and do not improve the yield. Higher temperature (130° - 135°C) favors formation of tetrabromodinitrobenzene.

ACKNOWLEDGMENT

Mr. J. D. Upton assisted in the experimental work covered by this report. Dr. O. H. Johnson, and Mr. Francis Taylor, Jr., also assisted in the pilot plant preparation of the s-dinitrotribromobenzene. Thermal stability data was taken by Mr. F. A. Greer and Mr. H. T. Simmons; crystal densities were determined by Mr. V. H. Galloway; and impact sensitivities were determined by the Explosives Properties Division of the Explosives Research Department.

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